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POROUS SYSTEMS FOR SUPER DENSE MEMORIES AND SENSOR APPLICATIONS

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14. ABSTRACT

This project was dedicated to solving basic scientific issues and developing the scientific basis that underlies the improvement of super-dense memories, towards the terabit per square inch goal and the engineering of chemical and biological sensors. Both applications rely on porous materials among which porous alumina is the most promising.

The research under this project in each of the objectives has lead to major advances. We have improved considerably the size distribution of the porous alumina used for masks using a double anodization process. We have also developed an unconventional "bootstrapping" method, which uses self-supporting porous membranes. This allowed fabrication and research on the properties of very well ordered array of small magnetic nanodots on different substrates, which could not be done otherwise. It also permitted us to develop new concepts of storage and explore the interaction between magnetic dots. Due to this technology we had also several major advances in the field of DNA sequencing and in the development of biosensors.

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ABSTRACT

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The research under this project in each of the objectives has lead to major advances. We have improved considerably the size distribution of the porous alumina used for masks using a double anodization process. We have also developed an unconventional "bootstrapping" method, which uses self-supporting porous membranes. This allowed fabrication and research on the properties of very well ordered array of small magnetic nanodots on different substrates, which could not be done otherwise. It also permitted us to develop new concepts of storage and explore the interaction between magnetic dots. Due to this technology we had also several major advances in the field of DNA sequencing and in the development of biosensors.

This project leverages funding from AFOSR through extensive collaboration with colleagues at UC San Diego, UC Davis and Los Alamos National Labs and no cost, contribution of researchers that are spending extended periods of times at UCSD.

EXECUTIVE SUMMARY

This project was dedicated to solving basic scientific issues and developing the scientific basis that underlies the improvement of super-dense memories, towards the terabit per square inch goal and the engineering of chemical and biological sensors. Both applications rely on porous materials. Among them porous alumina has demonstrated to provide major improvements in these two diverse applications.

At the beginning of this project we set the following objectives: a) to improve the geometry (regularity, shape, decreased size) of the pores, b) to fabricate and study the properties of nanostructured magnets in a variety of configurations and c) to apply this technology to chemical and biological sensing. These are forefront basic research topics and advances in them may lead to revolutionary changes in important technologies. This was already proven by earlier results from our group.

The research under this project in each of the objectives has lead to major advances. We have improved considerably the size distribution of the porous alumina used for masks using a double anodization process. We have also developed an unconventional "bootstrapping" method, which uses self-supporting porous membranes. This new method allowed us to fabricate and investigate in detail the properties of very well ordered array of small magnetic nanodots on different substrates, which could not be done otherwise. It also

permitted us to develop new concepts of storage and explore the interaction between magnetic dots. Due to this technology we had also several major advances in the field of DNA sequencing and in the development of biosensors.

This project leverages funding from AFOSR through extensive collaboration with colleagues at UC San Diego, UC Davis and Los Alamos National Labs. This project also benefits from the, no cost, contribution of researchers that are spending extended periods of times at UCSD. Graduate students and postdoctoral fellows are intimately involved in every aspect of this research.

I. ACCOMPLISHMENTS

As mentioned two major, important applications like development of terabit per square inch memory and bio-chemical sensors could benefit enormously from further basic understanding of the materials science, physics and chemistry of porous materials. Although the two applications are quite different the basis for both of them is a common technology; self-assembled porous materials. In particular, self-assembled porous alumina ***on a substrate*** . During this project we have made major improvements on the preparation and manipulation of porous alumina which consequently has given rise to advances in basic science areas like the understanding of: nanostructured magnets, microcapillary condensation and novel properties of confined organic materials. These advances have also lead to patented applications in magnetic storage and bio-chemical sensors.

Below we summarize the achievements during the project period in each of the initial objectives.

a) Improved Porous Materials

During the last period we have dedicated considerable efforts to improvements on the preparation of porous materials. We explore different approaches on the preparation of porous alumina samples to reach better pore regularity and to broaden the possible shapes that can be obtained. Three schemes were investigated; a) electron beam imprint lithography prior to the anodization to confer order and shape to the pores, b) two-stage anodization-evaporation at an angle method to create non-circular nanodots, and c) unconventional “bootstrapping” to confer order to the pore array without the need of expensive nanoimprint masks. These methods open up the possibility to investigate the properties of non-circular magnetic nanodots using characterization techniques such as neutron scattering or x-ray magnetic circular dichroism and permit the fabrication of complex nanostructures in macroscopic areas that can be used for sensing and confinement.

A very recent development was promised for a while, the so-called “bootstrapping” method. Originally the method makes use of iterative, anodization-nanoimprint mask preparation to improve the pore array distribution. The way we accomplished this is different than the original concept, but with better results. We use high-quality, large self-supported porous alumina as a mask and by means of reactive ion etching we transferred the ordered pattern to a supported aluminum thin film. A single short anodization performed on the aluminum film after this process shows a considerable improvement of the ordering and size distribution of the pores. This is quite exciting since unlike the original "bootstrapping" method this one does not require iterations or the preparation of an imprint mask which beside of being expensive quite often breaks. It also present a very competitive solution respect to the electron beam imprint since larger anodization areas can be improved with a much more inexpensive techniques.

Due to a large number of technical difficulties in using existing software for the characterization of nanostructures like porous alumina, we have developed a very flexible and useful program which allows automatically characterizing large areas images containing nanostructures. This technique is applicable to images generated by AFM, MFM, STM, SEM, etc. and is applicable to any system (including biologically relevant ones). While similar software is currently available, a number of difficulties make their application somewhat problematic. Some of the difficulties are caused by the discrimination of what is defined as the boundary between a structure of interest from the rest of the sample which cannot be easily accessed and changed. In addition, the analyses capabilities are very rudimentary, and the software is not very flexible so incorporating new analyses is difficult. All these limitations are solved in the new software which will be supplied free of charge to the community.

b) Nano Magnetic Arrays

In order to enhance storage capacity we developed and patented new ideas regarding multistate magnetic storage. One of them makes use of antiferromagnetic /ferromagnetic (AF/FM) bilayers exhibiting both negative and positive exchange bias. We have investigated these properties in thin film devices; now we are in the process of reducing these systems to the nanoscale in the x-y plane of the film to explore their magnetic properties. The AF/FM nanodots are fabricated using porous alumina masks as described above. This work was patented.

We have investigated the magnetic properties of dense arrays of magnetic rings. This type of systems may lead to new kinds of storage concepts and therefore understanding their behavior is crucial. In addition they are good prototype systems which allow the investigation of: 1) the magnetic interaction between nanostructures and 2) the ways to tune different magnetic states using external field. This is very important because eventually the magnetic storage not only will require making small structures but also understanding their interactions.

We have studied the magnetism of one-dimensional Fe chains in metallo phthalocyanines organic thin films. Making use of the particular stacking of these molecules, one-dimensional magnetic chains of variable lengths were grown and studied. In this fashion, we were able to determine the competition between intra-chain and inter-chain exchange interactions. More important this one-dimensional magnetic material is an excellent model system to test and understand the limitations of storage in reduced dimensionality.

c) Organic Materials- Confinement, Chemical and Biological sensors

Organic molecules may change their properties considerably when confined into small volumes. We have developed devices consisting of confined Cobalt-phthalocyanine molecules in porous alumina membranes supported on gold thin film to explore the modification of their electromagnetic properties by means of surface plasmon resonance experiments.

Organic molecules have been used as chemical and biological sensors in a variety of configurations. Very rapidly new electronic devices based on active organic materials are finding applications were silicon is not useful. In spite of these advances, the charge injection mechanism from metallic electrodes to the organic materials is still poorly understood. We have investigated in detail the limitations that growth methods impose on the charge injection mechanism. Our results show that thermal treatment (up to operation temperature) may

modify the properties of the interfaces especially regarding the diffusion of metals into the organic films.

A number of competitive schemes have been proposed for serial DNA sequencing. These include pulling DNA strands through a pore or laying down the strand on a substrate. In both the transverse resistance of each base is measured serially. All the serial sequencing methods have a serious, seemingly insurmountable, problem because the noise is much larger than the signal and therefore the noise swamps the interesting signal. We developed a method which enhances the signal to noise ratio considerably. The idea relies in using multiple, cross-correlations of the serial sequence measurement We showed using numerical simulations, that in this fashion the signal to noise ratio increases exponentially. The general idea has been disclosed in a patent application and a paper, which has been submitted for publication.

II. PRACTICAL RESULTS

The most recent results were summarized in a series of 12 papers in first-rate refereed journals, 3 patent applications, were part of 5 PhD theses, presented as invited and contributed talks at major meetings, and had a major influence on the education of graduate students and postdoctoral fellows.

This research has also been crucial in the education of several PhD students (Myroslavna Kovylyna, Anne Ruminski, Aida Serrano, Erez Tadmor, Yaniv Rosen, Ilya Valmiansky, Misha Erekhinsky, Ali Basaran) impacting their thesis work in different ways. Several postdoctoral fellows (Felix Casanova, Carlos Monton, Thomas Saerbeck) have contributed to the research outlined above. It is important to highlight that much of the research being done under this project benefits from extensive collaborations with chemist, physicists and engineers at UCSD and other institutions, thus the young investigators are exposed to an important modality of collaborative research.

The UCSD graduate students and postdocs associated with this project that have finished their tenure, are employed in industry, national labs and academia. They are also developing independent research in related fields. Several of the young collaborators are in the middle of their PhD studies or postdoctoral fellowships so some of the works were finished during their spare time since the funding ended before.

Archival Publications (published 8/1/10-7/31/13 – project entirety)

1. *The Fabrication of Ordered Arrays of Exchange Biased Ni/FeF$_2$ Nanostructures*, M. Kovylina, M. Erekhinsky, R. Morales, I.K. Schuller, A. Labarta and X. Battle, Nanotechnology, **21**, 175301 (2010)
2. *Development of Vortex State In Circular Magnetic Nanodots: Theory and Experiment*, J. Mejia-Lopez, D. Altbir, P. Landeros, J. Escrig, A.H. Romero, Igor V. Roschin, C.P. Li, M.R. Fitzsimmons, X. Battle and I. K. Schuller, Phys. Rev. B, **81**, 1 (2010).
3. *Asymmetric Magnetic Dots: A Way to Control Magnetic Properties,* N. M. Vargas, S. Allende, B. Leighton, J. Escrig, J. Mejia-Lopez, D. Altbir, and I. K. Schuller, J. Appl. Phys. **109**, 073907 (2011).
4. *Controlling Role of Nanopore Morphology in Capillary Condensation,* F. Casanova, C.E. Chiang, A.M. Ruminski, M.J. Sailor and I.K. Schuller, Am. Chem. Soc. **28**, 6832 (2012)

5. *Effect of Photodiode Angular Response on Surface Plasmon Resonance Measurements in the Kretschmann-Raether Configuration*, F. Galvez, C. Monton, A. Serrano, I Valmianski, J. De la Venta, I.K. Schuller and M.A. Garcia, Rev. Sci. InstruM. **83**, 093102 (2012)
6. *Interaction-induced Anisotropy in the Onion-to-Vortex Transition in Dense Ferromagnetic Nano-ring Arrays*, E. Tadmor, Y.J. Rosen, I.K. Schuller and S. Bar-Ad, J. Appl. Phys., **112**, 103903 (2012)
7. *The Role of Micro-shorts and Electrode-film Interface in the Electrical Transport of Ultra-thin Metallophthalocyanine Capacitive Devices*, C. Monton, I. Valmiansky and I.K. Schuller, Appl. Phys. Lett., **101**, 133304 (2012)
8. *Deconvoluting Reversal Modes in Exchange Biased Nanodots*, R.K. Dumas, C-P. Li, I.V. Roshchin, I.K. Schuller and K. Liu, Phys. Rev. B, **86**, 144410 (2012)
9. *Correlation Dynamics and Enhanced Signals for Serial DNA Sequencing*, T. Ahmed, J.T. Haraldsen, J.J. Rehr, M. DiVentra, I.K. Schuller and A.V. Balatsky, submitted to Nat. Nanotech. (2013)
10. *Charge Injection Across a Metal-Organic Interface Suppressed by Thermal Difussion*, C. Monton, T. Saerbeck, I. Valmianski and I.K. Schuller, submitted to Appl. Phys. Lett. (2013)
11. *Magnetism of Metal Phthalocyanines*, J. Bartolomé, C. Monton and I.K. Schuller, Chapter 9 in “Molecular Magnets”, NanoScience and Technology, Springer-Verlag, Berlin Heidelberg (2014)
12. *Microscopy Image Segmentation Tool: Robust Image Data Analysis*, I. Valmianski, C.M. Monton and I.K. Schuller, submitted for publication (2013)

Changes in research objectives, if any: None

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Extensions granted or milestones slipped, if any: None

Include any new discoveries, inventions, or patent disclosures during this reporting period (if none, report none):

<u>PATENTS</u>

1. *Exchange Biased Multi-state Magnetic Memory and Logic Devices and Magnetically Stabilized Magnetic Storage*, I.V. Roshchin, O. Petracic, R.Morales, Z.-P. Li, X. Batlle, I.K. Schuller, US Patent Number 7,764,454 2.

2. *Noise Reduction for DNA and other Macromolecules Sequencing Using Oversampling and Cross-Correlations,* I. K. Schuller, M. Di Ventra, A. Balatsky, UC Case No. SD2012-118

3. *Air-Standing Nanoporous Grid (ASNG),* C. Monton, I.K. Schuller, A.C. Basaran, UC Case No. SD2014-016